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STUDY 333: Protocol for Groundwater Protection List Monitoring for Methoxyfenozide, Chlorantraniliprole, and Flutriafol in High Use, Vulnerable Areas

INTRODUCTION

The objective of this study is to determine if methoxyfenozide, chlorantraniliprole, and flutriafol are migrating to groundwater in areas of their highest use on California agriculture. Recent detections suggest these three pesticides may have migrated to groundwater. In 2021, the Department of Pesticide Regulation (DPR) detected methoxyfenozide, chlorantraniliprole, and flutriafol in samples collected in DPR's Well Network Study (Davalos, 2022). This coincided with three previously reported detections of methoxyfenozide above 0.02 ppb by the United States Geological Survey from 2013 to 2020 (WIDB, 2021). DPR conducted follow-up monitoring and confirmed one of the reported detections above DPR's reporting limit of 0.03 ppb and three trace detections. All wells that are part of the Well Network Study were sampled for these three analytes in 2022. The results of the Well Network Study for these analytes will be reported along with findings of this study.

Section 13148 of the California Food and Agricultural Code of the Pesticide Contamination Prevention Act (PCPA), directs DPR to monitor groundwater for pesticides designated as having the potential to pollute groundwater. DPR identifies, in code, these pesticides as the Groundwater Protection List (GWPL, Title 3 California Code of Regulations [3CCR] section 6800 [a and b]). Chlorantraniliprole is listed on the GWPL. Methoxyfenozide and flutriafol have Specific Numerical Values (SNVs)[1] that meet criteria to be listed on the GWPL but have not

[1] Specific Numerical Values (SNVs) are used as thresholds by DPR to determine potential risk of groundwater contamination posed by agricultural use pesticides. (www.cdpr.ca.gov/docs/emon/grndwtr/regs/contaminants.htm).

been added since the last update of the regulation. Table 1 shows the pesticides' chemical characteristics. Their SNVs indicate that the pesticides are both mobile and persistent in soil.

Table 1. SNV thresholds and methoxyfenozide, chlorantraniliprole, and flutriafol physical-chemical properties.

	Mobility		**Persistence**		
	Water solubility mg/L	Koc (cm^3/g)	Hydrolysis (day)	Aerobic soil metabolism (day)	Anaerobic soil metabolism (day)
SNV	> 3	< 1900	> 14	> 610	> 9
Methoxyfenozide	3.3	219-922	1572	336-722	654
Chlorantraniliprole	1.02	85-758	9.9	220-554	165-220
Flutriafol	95.3	123-395	30	532-1210	100

Methoxyfenozide and chlorantraniliprole are insecticides and flutriafol is a fungicide. Table 2 shows the total reported agricultural use of each active ingredient (AI) in California and Figure 1 shows the reported use per year of AI. The agricultural use of the three AIs has steadily increased since they were registered for use in California. Combined with increased use (Figure 1), low binding affinity to soil organic matter, and high persistence in soil (Table 1), methoxyfenozide, chlorantraniliprole, and flutriafol have the potential to contaminate groundwater.

Table 2. Total amount of agricultural use of methoxyfenozide, chlorantraniliprole, and flutriafol use since their registration in California.

Active Ingredient	**Period of used**	**Amount used (lb)**
Methoxyfenozide	2003-2021	5,400,000
Chlorantraniliprole	2008-2021	1,480,000
Flutriafol	2015-2021	72,000

OBJECTIVES

The purpose of this study is to determine whether methoxyfenozide, chlorantraniliprole, and flutriafol have migrated to groundwater in areas of California with high reported agricultural use that have been identified as vulnerable to groundwater contamination. In high use areas, groundwater samples may also be collected and analyzed for additional pesticides known to, or with the potential to, contaminate groundwater, such as metolachlor, chlorthal-dimethyl (Dacthal), and their degradates. Other pesticides and degradates on the GWPL that are included in DPR's analytical screens will also be analyzed during this monitoring study.

PERSONNEL

Well sampling will be conducted by the Environmental Monitoring Branch of DPR under the general supervision of Groundwater Protection Program's (GWPP) Supervisor, Carissa Ganapathy.

Project personnel will include:

Project Leaders:	Majid Afyuni, Ph.D., and Craig Nordmark
Field Coordinator:	Andrew Hawkins
Senior Scientist:	Rick Bergin
Laboratory Liaison:	Vaneet Aggarwal, Ph.D.
Analytical Chemistry:	Center for Analytical Chemistry, California Department of Food and Agriculture (CDFA)

Please direct questions regarding this study to Majid Afyuni by email at majid.afyuni@cdpr.ca.gov or Craig Nordmark at craig.nordmark@cdpr.ca.gov.

STUDY PLAN

This study will be conducted in high use areas of methoxyfenozide, chlorantraniliprole, or flutriafol to determine if agricultural use is resulting in contamination of groundwater. Figure 2 shows the nine counties with the highest reported agricultural use of each AI. Fresno County has the greatest use of the three AIs. Approximately 84% of methoxyfenozide, 75% of chlorantraniliprole, and 74% of flutriafol applications in California occur in the nine counties. Other counties have some high use sections even though the total use in the county is low. (CDPR, 2022).

Across the State, but mostly in the counties of greatest use, sections will be compared and prioritized for monitoring based on the following factors:

1. High methoxyfenozide, chlorantraniliprole, or flutriafol use levels within the section. Moderate levels of at least two of the target pesticides in the section or within the surrounding sections will be used to narrow down additional areas
2. Shallow average depth-to-water within the section based on historical levels
3. Previously reported detections of any pesticides in wells within or surrounding the section
4. Sections that are identified by DPR as Ground Water Protection Areas
5. Available wells to sample based on existing records in the Well Inventory Database

SAMPLING

Wells will be selected in the designated areas following procedures described in SOP FSWA001.04 (Kocis, 2022). Domestic wells will be prioritized for sampling because they are typically accessible year-round and tend to be shallower than irrigation or municipal wells. During collection of groundwater samples, all efforts will be taken to bypass pressure tanks, hoses, and filters to sample water directly from the aquifer as outlined in FSWA001.04.

ANALYTICAL METHODS

Chemical analysis will be performed by CDFA's Center for Analytical Chemistry. CDFA will analyze samples for chlorantraniliprole, flutriafol, and methoxyfenozide using the Multi-Analyte Screen, method number EMON-SM-05-032 (CDFA, 2022). Well samples will also be analyzed using the Triazine Screen, method number EMON-SM-62.9 (CDFA, 2020). When areas of high use of the three pesticides coincide with high levels of chlorthal-dimethyl or metolachlor use, CDFA laboratory will analyze additional samples for chlorthal-dimethyl and/or metolachlor. CDFA will analyze for chlorthal-dimethyl, MTP, and TPA using method EMON-SM-05-040 (CDFA, 2016). Metolachlor, metolachlor ESA, and metolachlor OXA will be analyzed using EMON-SM-05-034A (CDFA, 2022). A list of all pesticides to be analyzed and their respective reporting limits are listed in Tables 3 to 5. GWPP staff will follow the guidelines in SOP QAQC001.01 (Peoples, 2019) for analytical laboratory quality control and for collecting quality assurance samples in the field. DPR has determined that the analytical methods used for this study provide unequivocal identification of the chemicals (Aggarwal, 2017; Aggarwal, 2020; Aggarwal, 2022a; Aggarwal, 2022b).

Table 3. Multi-Analyte Screen (LCMS) method detection limits (MDL) and reporting limits (RL) in ppb (µg/L) (EMON-SM-05-032, Revision 2) (CDFA, 2022).

Analyte	**MDL**	**RL**
Alachlor	0.00920	0.03
Atrazine	0.00286	0.02
Azinphos-methyl	0.01440	0.05
Azoxystrobin	0.00584	0.02
Bensulide	0.00571	0.02
Bromacil	0.00393	0.02
Carbaryl	0.00323	0.02
Carbofuran	0.00393	0.02
Chlorantraniliprole	**0.00345**	**0.02**
Cyprodinil	0.00427	0.02
Diazinon	0.01050	0.03
Dimethenamide	0.00490	0.02
Dimethoate	0.00330	0.02
Diuron	0.00484	0.02
Ethofumesate	0.00845	0.03
Fenamiphos	0.01070	0.03
Fludioxonil	0.00892	0.03
Flutriafol	**0.00298**	**0.02**
Imidacloprid	0.00323	0.02
Isoxaben	0.00493	0.02
Linuron	0.00697	0.02
Mefenoxam/metalaxyl	0.00295	0.02
Methiocarb	0.00710	0.02
Metolachlor	0.01660	0.02
Methomyl	0.00301	0.02
Methoxyfenozide	**0.00628**	**0.03**
Metribuzin	0.00414	0.02
Napropamide	0.00462	0.02
Norflurazon	0.00550	0.02
Oryzalin	0.01140	0.05
Prometon	0.00245	0.02
Propiconazole	0.00424	0.02
Pyraclostrobin	0.00210	0.02
Simazine	0.00279	0.02
Tebuthiuron	0.00524	0.02
Thiamethoxam	0.00386	0.02
Thiobencarb	0.00245	0.02
Uniconazole	0.01370	0.05

Table 4. Multi-Analyte Screen (GCMS) method detection limits (MDL) and reporting limits (RL) in ppb (µg/L) (EMON-SM-05-032, Revision 2) (CDFA, 2022).

Analyte	MDL	RL
Clomazone	0.00799	0.05
Dichloran	0.01103	0.05
Dichlobenil	0.00678	0.03
Disulfoton	0.01040	0.05
Ethoprophos	0.00506	0.03
Fonofos	0.00616	0.03
Malathion	0.00691	0.03
Parathion ethyl	0.00646	0.03
Parathion methyl	0.00655	0.03

Table 5. Triazine Screen method detection limits (MDL) and reporting limits (RL) in ppb (µg/L). (Method EMON-62.9, revision 5) (CDFA, 2020).

Analyte	MDL	RL
Deisopropyl-atrazine or Deethyl-simazine (ACET)	0.00580	0.03
Atrazine	0.00316	0.02
Bromacil	0.00241	0.02
Diaminochlorotriazine (DACT)	0.00235	0.05
Deethyl-atrazine (DEA)	0.00226	0.02
Diuron	0.00241	0.02
Desmethyl-norflurazon (DSMN)	0.00181	0.01
Hexazinone	0.00197	0.01
Metribuzin	0.00238	0.05
Norflurazon	0.00252	0.02
Prometon	0.00240	0.02
Prometryn	0.00265	0.05
Simazine	0.00286	0.02
Tebuthiuron	0.00236	0.05

DATA ANALYSIS

Data obtained from the well samples analyzed will be used by GWPP to determine if pesticides are migrating to groundwater in areas of agricultural use. These data will also be used to generate a study report detailing the results. Detections in the targeted and surrounding areas will be used to assess regional vulnerability to groundwater contamination. These results may trigger additional sampling, lead to expansion of Ground Water Protection Areas, or formal review of a detected pesticide as outlined in Food and Agricultural Code sections 13149-13151. Results from this study will be published to the Well Inventory Database during the annual update.

TIMETABLE

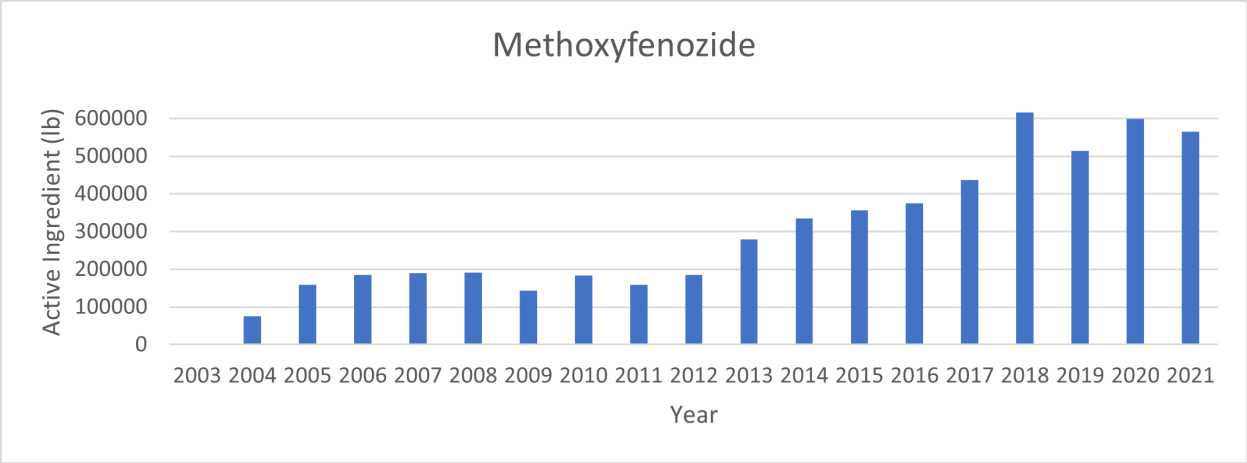
July 2022 – December 2022:	Conduct sampling
September 2022 – June 2023:	Obtain and review analytical results from CDFA laboratory
March 2024:	Complete study report

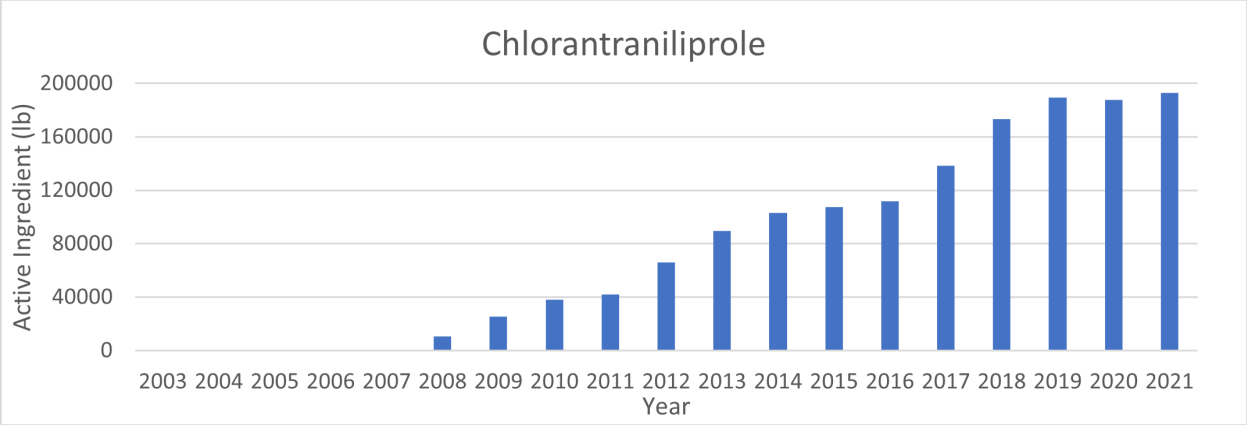
COMMUNICATION

- Provide notice to the County Agricultural Commissioner, DPR Enforcement Branch Regional Office, and the local Farm Bureau two weeks prior to initiating monitoring in a county. Additional notice will be provided if there is a six-month lapse in monitoring within a county.
- Provide results to participating well users within 60 days of receipt from the laboratory.
- Provide a summary of results to the County Agricultural Commissioners and the County Environmental Health Officers when sampling is concluded, and results have been reviewed and approved by DPR.
- Results will be published to the Well Inventory Database during the annual update.
- A final report will be prepared at the conclusion of the study and posted to DPR's website.

FIGURES

Figure 1. Statewide reported agricultural use of methoxyfenozide, chlorantraniliprole, and flutriafol in pounds (lb) per year (CDPR, 2022). The scales for each graph are different.





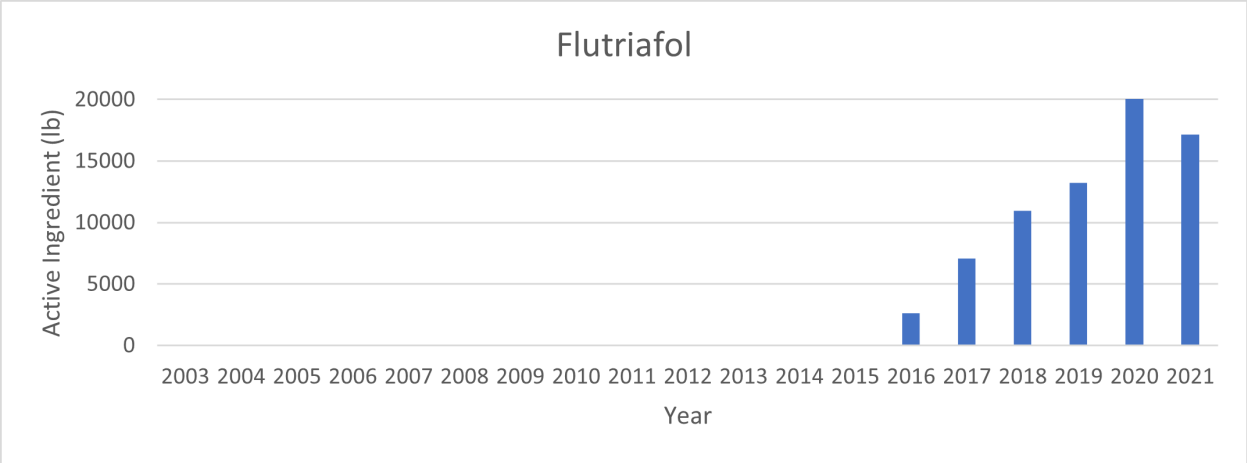
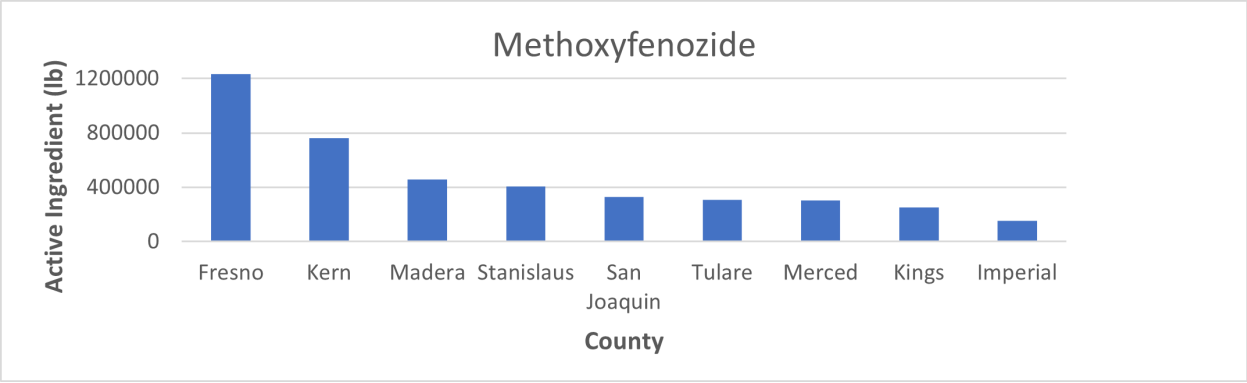
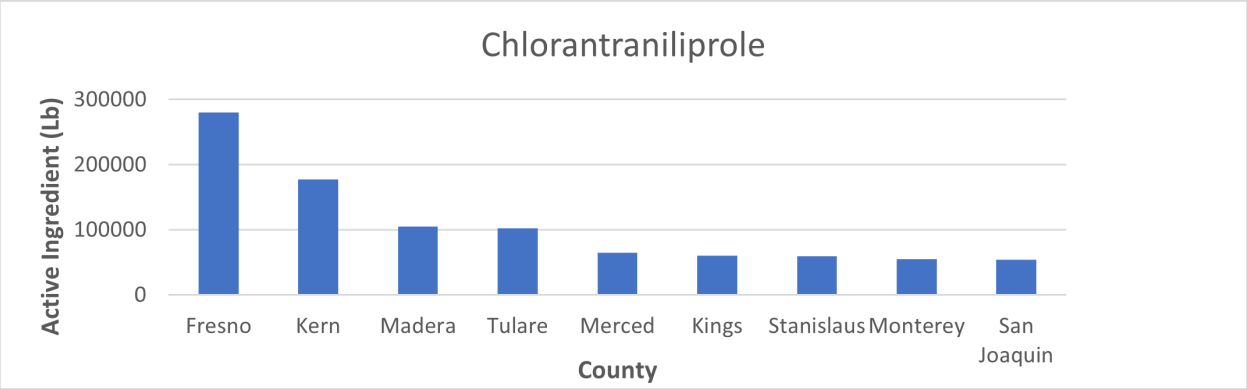
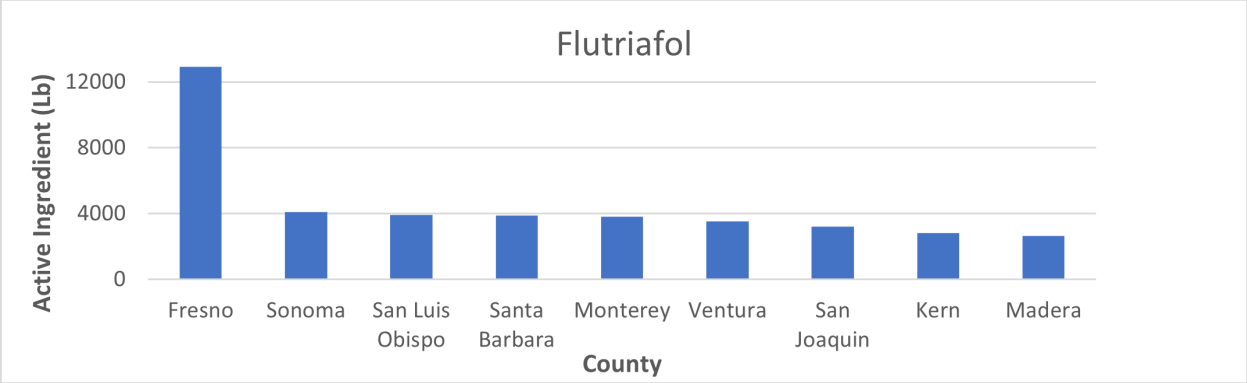


Figure 2. Total reported agricultural use of methoxyfenozide, chlorantraniliprole, and flutriafol for the nine highest-use counties (CDPR, 2022). The scales on each graph are different.







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